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Development of gas sensors using ZnO nanostructures

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Abstract. Different ZnO nanostructures such as nanowires, nanobelts and tetrapods have been grown and used for preparation of thick film (with random grain boundaries) as well as isolated nanowire/nanobelt gas sensors. Sensitivity of different type of sensors has been studied to H_2S and NO gases. The results show that the response of ZnO sensors to H_2S arises from grain boundary only whereas both grain boundaries and intragrain resistances contribute towards response to NO. In addition, oxygen vacancies in the lattice were also seen to help in improvement of sensor response. Room temperature operating H_2S and NO sensors based on ZnO nanowires have been demonstrated. Further, sensors based on isolated nanobelts were found to be highly selective in their response to NO.

Keywords. Gas sensors; nanowires; ZnO; tetrapods; NO; H_2S.

1. Introduction

Semiconductor metal-oxide based gas sensors are commonly used for environmental monitoring and industrial applications due to their advantages such as small dimensions, low cost and convenient operation.[1,2] The gas sensing mechanism of these sensors involves adsorption of atmospheric oxygen on the oxide surface that extracts electrons from the semiconducting material leading to change in carrier density and conductivity. On interaction with oxidizing or reducing gases, adsorbed oxygen concentration and thereby conductivity changes. The change in conductivity is a measure of gas concentration. For reducing gases such as H_2S and NH_3 the conductivity increases for *n*-type materials (as SnO_2 and ZnO) and reduces for *p*-type materials (as Te). The effect of oxidizing gases is opposite to that of reducing gases. Since the gas sensing mechanism is a surface reaction, use of nanostructured materials is expected to improve gas sensing characteristics.

Among the semiconductor metal oxides, zinc oxide (ZnO) is one of the most widely used gas sensing material.[3–6] In this report, we present the work done in our laboratory on the growth of ZnO nanostructures by thermal evaporation technique and investigation of their gas sensing properties. The studies aim at (a) development of sensors with better sensitivity and room temperature operation provided by increased surface area, (b) single nanowire sensors with a view to miniaturize them, (c) comparison of the sensing characteristics of single nanowires and films made using nanowires to clearly differentiate the intragrain and grain boundary contributions as well as to develop sensors with better sensitivity/selectivity. It is found that (i) both intragrain and grain boundary regions contribute to sensitivity, (ii) for different gases either of the two responses may be higher leading to possibility of improved selectivity and (iii) depending on growth conditions, changes in crystalline defects may improve sensitivity.

2. Experimental

2.1 *Growth of nanostructures*

ZnO nanostructures were prepared in a horizontal tube furnace having facility for introducing gases at controlled rates. In the initial experiments, pure Zn metal powder was heated to temperatures between 600 and 900°C under argon atmosphere (flow rate 500 cc/min) and on stabilizing the temperature at desired value, the gas atmosphere was switched to 95% argon and 5% oxygen. ZnO nanowires (<100 nm diameter) and thicker nanowires called nanorods (~500 nm dia) were obtained at source itself at temperatures of 700 and 800°C respectively. At source

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temperature of 900°C, nanowires of 100–500 nm diameter were deposited on substrates placed in downward gas flow direction at temperature of 200°C. For growth of tetrapods and long nanowires required for isolated nanowire experiments, a mixture of ZnO and graphite in 3 : 1 ratio (by weight) was heated to 1050°C (at a rate of 6°C/min) under argon atmosphere.[7] While heating, 2–5% oxygen was added to argon gas at temperatures between 800 and 1050°C. Nature of nanostructures mainly depended on the temperature at which oxygen was introduced (which controls the nature of nuclei formed). Nanowires and nanobelts were obtained in case of oxygen introduction at 800–950°C and tetrapods in case of oxygen introduction at 950–1050°C. All nanostructures were deposited on substrates maintained at temperatures from 200 to 450°C.

2.2 *Preparation of sensors*

Two different type of sensors were prepared, (a) thick films of nanostructures (NS) and (b) isolated nanowires/belts. For thick films, the nanostructures were dispersed in suitable organic solvents and deposited on alumina substrates. This was followed by heating to temperatures of 200–400°C and deposition of gold contacts. In some cases nanowires were directly grown on substrates with pre-deposited thick film gold contacts. Isolated nanowires/belts based sensors were prepared by dielectrophoresis[8] technique, where, gold electrodes with a spacing of 25 μm were deposited on alumina substrates by thermal evaporation. An ac voltage of 20 V (peak to peak) at 100 kHz was applied to the electrodes and a suspension of nanowires/nanobelts (NS) in methanol (0·1 mg NS in 10 ml of methanol) was put drop-wise between them. Typically, 5–10 drops of suspension were put on a substrate over a period of 20 min. The samples were examined using SEM and those consisting of one or few NS between two electrodes were selected for measurement of response to gases.

2.3 *Characterization*

Surface morphology of the samples was studied using a scanning electron microscopy (SEM), chemical composition was determined by Energy Dispersive X-ray analysis (EDX) technique and the phases present were identified by X-ray diffraction (XRD). Photoluminescence measurements were performed to investigate lattice defects in the material. For measurement of response to gases, the sensors were loaded in an airtight housing having a volume of 250 cm^3. A measured quantity of gas at 1000 ppm concentration was introduced in the housing using a syringe and resistance of the samples was measured as a function of time.[9]

3. Results and discussion

Three different kind of nanostructures, i.e. tetrapods, nanowires and nanobelts as shown in figure 1 were used for preparation of sensors. Nanowires and nanobelts were usually obtained as a mixture. Diameter of different nanowires and legs of tetrapods varies from 50 to 150 nm range. Five different kind of sensors (Zn1 to Zn5) that were fabricated are: (a) thick film tetrapods (Zn1) and nanowires (Zn2) directly deposited on alumina substrates, (b) nanowires dispersed on substrates to yield thick film (Zn3) followed by annealing, (c) isolated few (2 to 8) nanowires or nanobelts aligned between two electrodes (Zn4) using dielectrophoresis technique and (d) using polycrystalline ZnO powder sensors (Zn5). Isolated nanowires/belts in Zn4 type sensors are shown in figure 1. Nanowires for sensors Zn2 were deposited using Zn metal source and all other sensors (except polycrystalline material) were prepared using nanostructures obtained by using ZnO and graphite mixture.

XRD (spectra not shown here) and EDX measurements carried out on different materials showed pure ZnO material. Photoluminescence (PL) measurements were carried out to investigate structural defects and impurities in different materials. Figure 2 shows the room-temperature photoluminescence (PL) spectra recorded for ZnO nanorods, nanotetrapods and polycrystalline material.[7] For nanorods, two peaks are observed: an UV band at 380 nm and a green band at 475 nm. UV band emission of ZnO is understood to be due to direct recombination of electrons in Zn 4p conduction band with holes in O 2p valence band, while the green emission has been suggested to be due to the presence of various point defects (oxygen vacancies).[7] It is seen that ZnO nanorods have higher concentration of oxygen vacancies compared to polycrystalline sample (inset). For tetrapods, a single absorption band with peak at 475 nm is observed indicating much higher defect density.

Typical response of ZnO nanowires (Zn2), tetrapods (Zn1) and polycrystalline material (Zn5) to

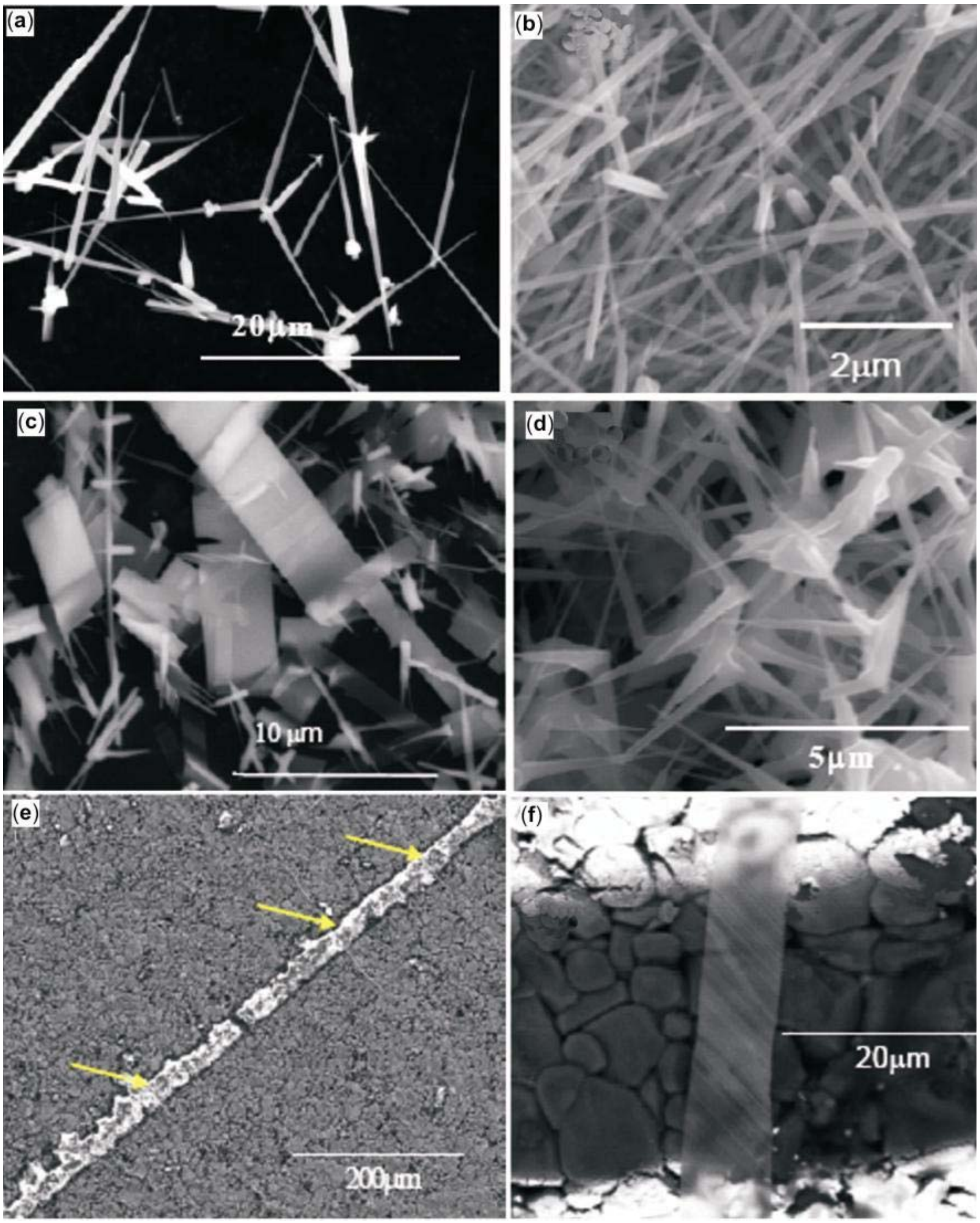

Figure 1. Scanning electron micrographs of (**a**) ZnO nanotetrapods, (**b**) nanowires, (**c**) nanobelts and (**d**) tetrapods film deposited on alumina substrate (Zn1 sensors). Isolated nanostructures aligned between gold electrodes with 25 μm separation: (**e**) three nanowires/belts shown by arrows and (**f**) a nanobelt. All of the structures shown in this figure have been prepared by using ZnO and graphite source.

4 ppm of H_2S gas measured at room temperature is shown in figure 3. Here, response is defined by:

$$S = 100 \times \left| \frac{Ra - Rg}{Ra} \right| . \qquad (1)$$

Data in figure 3a show that tetrapods have maximum while polycrystalline material has minimum sensitivity to H_2S. Response of tetrapods to different concentration of the gas (figure 3b) shows that the films fully recover to original resistance after exposure to the gas. The films were found to be sensitive to 1 ppm and lower concentration of H_2S. Relative response of different type of materials may be understood with reference to the PL data. Oxygen vacan-

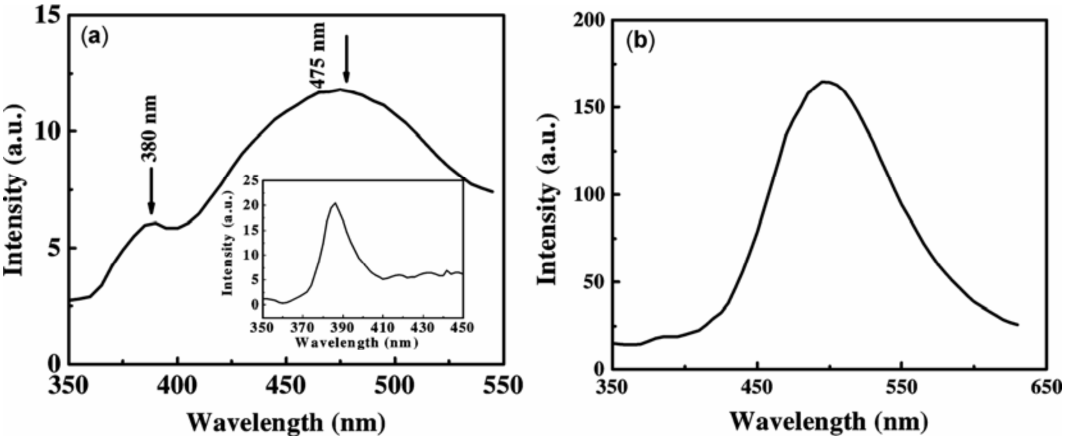

Figure 2. Photoluminescence spectra of (**a**) ZnO nanorods and (**b**) nanotetrapods. Inset of figure (**a**) shows PL spectra of polycrystalline powder.

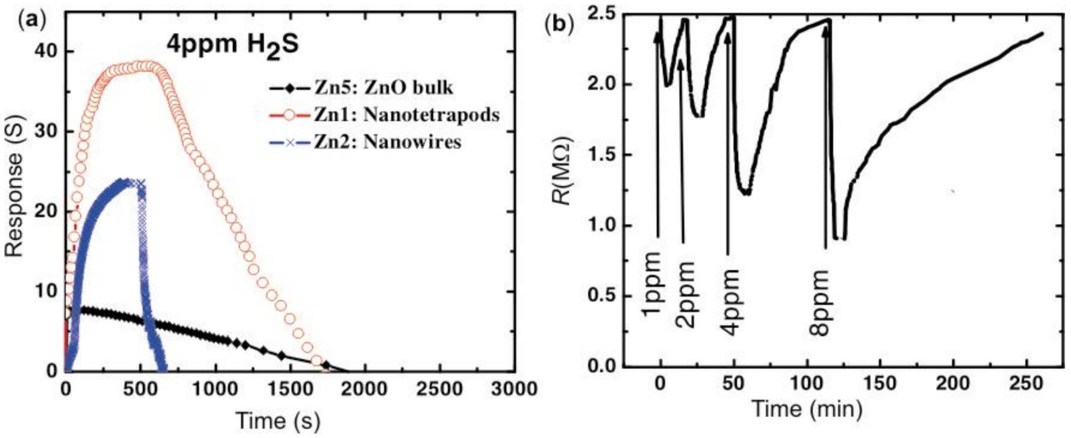

Figure 3. (**a**) Response of Zn1, Zn2 and Zn5 sensors to H_2S gas at room temperature and (**b**) time dependence of resistance of a Zn1 type sensor on exposure to different concentrations of H_2S.

cies and defects in lattice act as adsorption sites for oxygen. As the detection of gases originates from interaction of these adsorbed oxygen atoms with reducing gases such as H_2S, maximum (minimum) defect density in tetrapods (polycrystalline material) yields maximum (minimum) response. Smaller size of nanowires and tetrapods may also contribute to their better response.

Typical response of Zn3 type thick film nanowire sensors to H_2S is shown in figure 4. Five sensors were tested and similar results were obtained for other sensors. These thick films had typical room temperature resistance (in air) of 500 MΩ. Comparison with Zn1 and Zn2 sensors shows that (a) sensitivity or relative change in resistance on exposure to same concentration of gas is significantly higher and (b) initial resistance in air is higher. These results can be understood as in this case the nanowires have been dispersed from organic solution leading to poorer connectivity between nanowires. This leads to higher initial resistance as well as increased contribution to response from grain boundary region. As seen later, response to H_2S arises only from grain boundary resistance. For comparison response of Zn3 sensors to NO gas is also shown in figure 4. It is seen that dispersed nanowires have good response to both H_2S and NO gases.

Response of Zn4 samples (isolated NS) was tested to different gases. The results showed (a) the samples having only nanowires had no response to NO, H_2S, NH_3, CO and CH_4 gases and (b) samples having one or more nanobelts had good response to NO but less than 1% change in resistance on exposure to other gases including H_2S. High sensitivity of nano-

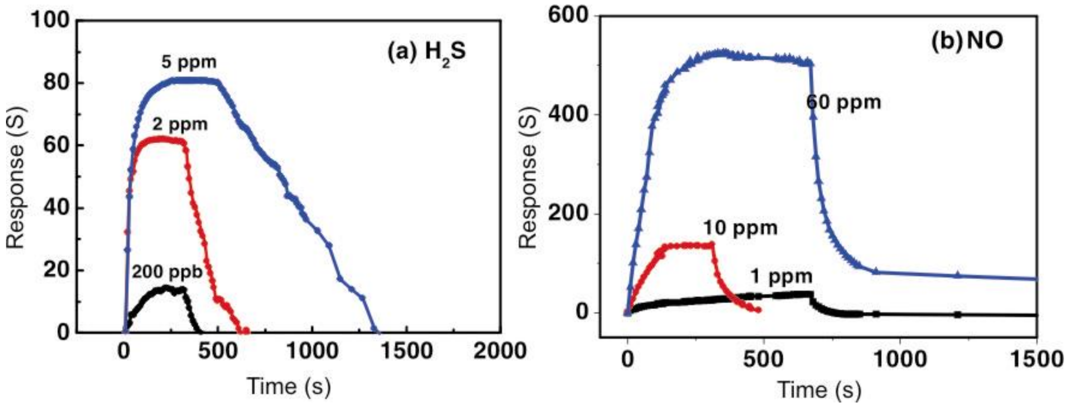

Figure 4. Response and recovery curves of typical Zn3 type sensors to different concentration of (**a**) H_2S and (**b**) NO gas.

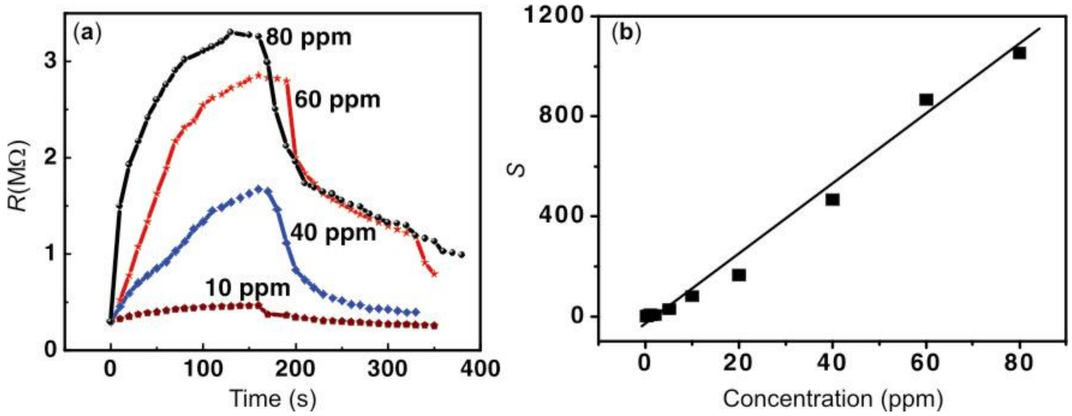

Figure 5. (**a**) Resistance of a typical Zn4 sensor with nanobelts on exposure to NO gas at different concentrations and (**b**) response as a function of concentration.

belts (for NO) compared to nanowires may partly arise due to their small thickness (<20 nm) in comparison to (~ 100 nm) diameter of nanowires that yields larger surface to volume ratio. Effect of exposure to different concentration of NO and response versus concentration characteristics for a typical sensor are shown in figure 5. The sensitivity of these sensors to NO is quite similar to that of Zn3 sensors. The results show that the response of ZnO to H_2S arises only from change in resistance of grain boundaries (that are absent in Zn4 sensors) while that to NO is contributed both by intragrain and grain boundary resistances. Impedance spectroscopy measurements to confirm these findings are being carried out. The results may be compared with those reported by us on gas sensing characteristics of tellurium (a *p*-type semiconductor), where oxidizing gas chlorine has larger influence on grain boundary resistance and reducing gas H_2S has higher contribution from intragrain regions.[10] Further studies are necessary to understand detailed mechanism of these differences in response from intragrain and grain boundary regions.

The above results show that lattice defect as oxygen vacancies influence the response of ZnO sensors to H_2S. It is seen that the response of ZnO to H_2S is mainly contributed by change in grain boundary resistance and that to NO by both intragrain and grain boundary resistance. Isolated wire sensors, having no grain boundaries provide highly selective response to NO gas.

4. Conclusions

The effect of microstructure on response of *n*-type semiconductor ZnO to H_2S and NO gases has been investigated. It is seen that the response to H_2S arises due to changes in grain boundary resistance while that to NO arises due to changes in both intragrain and grain boundary resistances. The results may be compared on *p*-type semiconductor Te, where response to oxidizing gases is mainly contributed by grain boundary resistance. Oxygen vacancies in the lattice were also seen to help in improvement of sensor response. Room temperature operating H_2S and NO sensors based on ZnO nanowires have been demonstrated.

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